

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improvements relating to Luminescent Materials

We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2. a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a luminescent material, to a luminescent screen and to a source of radiation containing such a material.

Luminescent materials are used in many applications to convert electromagnetic or corpuscular radiation into light. In accordance with the particular application, a luminescent material having a wide spectrum or a spectrum in which the emission is restricted to one or more narrow wavebands will be chosen. In practically all applications, it is desirable that the efficiency of the above-mentioned conversion should be high. Sometimes the temperature-dependence of the luminescent material is important, where the temperature-dependence of the material is understood to mean the relationship between the temperature of the material and the light output per unit of input energy. In some applications, for example, in high-pressure discharge lamps, the luminescent material is used in a screen which is at a high temperature in operation, for example from 300°C to 600°C. It is desirable for the light radiation from the luminescent screen to be high at these temperatures. Many known luminescent materials do not satisfy this last-mentioned requirement. They often have a satisfactory light output at room temperature, but this output falls off considerably as the temperature rises, this trend is particularly apparent above 100°C.

The present invention provides a luminescent substance consisting of an activator and a borate of at least one of the alkaline earth metals selected from the group consisting of calcium, strontium and barium, wherein the activator is terbium or terbium and gad-

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olinium wherein the molar ratio between the total quantity of alkaline earth metal and the quantity of boron trioxide lies within the range from 1:3 to 4:1 and wherein the total quantity of activator is from 0.02 to 0.4 gm.atoms/mole. of boron trioxide.

When the luminescent substances according to the present invention are suitably excited, they exhibit green luminescence; detailed examination shows that this green light consists of strong emissions in a number of narrow wavebands. The maxima of these wavebands are at different wavelengths and the strongest emission peak is found at about 545 mμ. Owing to this pronounced green colour of the emitted radiation, these luminescent substances cannot be used alone for general illumination purposes, but they may be employed in mixtures with luminescent materials emitting radiation in other parts of the spectrum, so that by choosing a suitable composition of these mixtures, substantially white light is produced. The most important uses of the luminescent substances according to the present invention are for applications where a radiation in a narrow waveband is desired. Such applications include photo-printing lamps, lasers, plant irradiation devices, devices for controlling chemical reactions and cathode-ray tubes for the reproduction of colour pictures. In these applications, the lamps are often enclosed in small spaces, so that the luminescent material quickly reaches a high temperature. Under these conditions, a good temperature-dependence of the luminescent substance is important.

Since many luminescent substances according to the present invention have a satisfactory temperature - dependence, they may be used quite successfully in a high-pressure mercury discharge lamp in which the discharge tube is surrounded by an envelope which is coated with a luminescent substance. A considerable proportion of the electrical energy supplied to a high-pressure mercury discharge tube is

converted into heat. As a result the temperature of the envelope surrounding the discharge tube increases. Depending on the size of the envelope and the power supplied to the discharge tube, the temperature of the envelope is usually between 300°C and 600°C. For a series of discharge lamps which have the same power inputs, the envelope temperature will be higher for the lamps which have smaller envelopes.

Since the luminescent substances of the present invention have low melting points, they may also be satisfactorily used as laser material, since they can be readily shaped in the desired form.

The quantity of activator is preferably chosen to be from 0.03 to 0.3 gm. atoms/mol. boron trioxide, since then the highest light outputs are attained. The quantity of gadolinium may be from 0.05 to 0.25 gm. atoms/mol. boron trioxide.

The use of gadolinium as part of the activator provides the advantage that less terbium need be used. A large quantity of terbium in the luminescent substance may give rise to concentration quenching of the light output from the substance. By adding gadolinium, higher light outputs may be obtained. The colour of the emitted radiation is substantially not changed by the use of gadolinium. Apparently, the gadolinium provides a transfer of excitation energy to the terbium. An

additional advantage of the use of gadolinium is that the cost price of the luminescent substances is lower, since gadolinium is considerably cheaper than terbium.

A number of examples are given for different compositions of luminescent substances in Tables I to VI below. The first column of the Tables indicates the alkaline earth metal oxides employed and the molar ratio of these oxides to the boron trioxide. The Tables furthermore indicate the quantity of activator employed, the relative light output at room temperature and the light output measured at 400°C and 500°C as a percentage of the light output at room temperature. The light output at room temperature is measured relative to a standard luminescent powder consisting of manganese and antimony activated calcium halophosphate mixed with calcium carbonate so that the light output is reduced to 54% of the initial light output of the calcium halophosphate. For comparison, the known red luminescing magnesium arsenate, activated with manganese, with respect to the above standard, has a light output of 87%. All measurements were made with the excitation of the luminescent substances by a radiation of a wavelength of 253.7m $\mu$ . In the compositions listed in Tables IV, V and VI, the constituents of the mixtures of alkaline earth metal oxides were each used in equimolar proportions in the respective mixtures.

TABLE I

Molar ratio CaO : B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Quantity of Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400°C.	at 500°C
3 : 1	0.06	—	42	64	59
3 : 1	0.12	0.12	64	106	54
3 : 1	0.06	0.06	76	102	63
3 : 1	0.06	0.12	78	96	90
3 : 1	0.06	0.24	68	93	83

TABLE II

Molar ratio SrO : B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Quantity of Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400°C	at 500°C
3 : 1	0.12	—	141	64	17
3 : 1	0.12	0.12	52	75	22
3 : 1	0.06	0.06	100	68	30
1 : 1	0.12	—	76	121	125

TABLE III

Molar ratio BaO : B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Quantity of Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400°C	at 500°C
1 : 1	0.06	—	57	120	126
1 : 1	0.06	0.12	26	155	157
1 : 2	0.06	—	34	116	126

TABLE IV

Molar ratio (CaO + SrO) : B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Quantity Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400°C	at 500°C
3 : 1	0.06	0.12	79	85	30

TABLE V

Molar ratio (BaO + SrO) : B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Quantity of Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400°C	at 500°C
3 : 1	0.06	0.12	83	71	42
1 : 1	0.06	0.12	54	116	113

TABLE VI

Molar ratio (CaO + BaO + SrO):B <sub>2</sub> O <sub>3</sub>	Quantity of Tb in gm. atoms/ml. B <sub>2</sub> O <sub>3</sub>	Quantity of Gd in gm. atoms/mol. B <sub>2</sub> O <sub>3</sub>	Relative light output at room temperature	Light output in % of the light output at room temperature	
				at 400 °C	at 500 °C
1 : 1	0.06	—	60	117	121

From the Tables, it will be seen that some of these substances exhibit a higher light output at higher temperatures than at room temperature. It is furthermore apparent from the Tables that the light output of some of the other substances is much lower at the higher temperatures than at room temperature; since some substances according to the present invention were found to have a high light output at room temperature, these lower light outputs at high temperatures need not be disturbing. The product of the light output at the operating temperature expressed in % of the light output at room temperature and the relative light output at room temperature is a measure of the suitability of a particular substance for each application. Since the light output at room temperature may often be improved by an improved method of manufacture, the possibility is not excluded that the luminescent substances according to the present invention may exhibit a considerably higher light output than the values indicated in the Tables.

By way of example a method of manufacturing a substance according to the invention will now be described for the manufacture of calcium borate, activated with terbium, with a composition defined in the first line of Table 1.

*Example:* A mixture of 5.70 gms of CaCO<sub>3</sub>, 2.50 gms of H<sub>3</sub>BO<sub>3</sub>, and 0.23 gm of Tb<sub>2</sub>O<sub>3</sub> was prepared and was then heated in a crucible of ceramic material between 600°C and 700°C for some time in order to expel the water from the H<sub>3</sub>BO<sub>3</sub>. Then heating is continued in air for two hours in order to complete the reaction to form the luminescent substance. In certain cases it is desirable to refine the product obtained after sintering and to heat it again in air for two hours. If necessary, this is repeated. The reaction mixture is heated preferably at a temperature only just below the melting

point of the borates. Other luminescent substances according to the invention, including substances having compositions indicated in the Tables, may be manufactured in a similar manner.

#### WHAT WE CLAIM IS:—

1. A luminescent substance consisting of an activator and a borate of at least one of the alkaline earth metals selected from the group consisting of calcium, strontium and barium, wherein the activator is terbium or terbium and gadolinium, wherein the molar ratio between the total quantity of alkaline earth metal oxide and the quantity of boron trioxide lies within the range from 1:3 to 4:1 and wherein the total quantity of activator is from 0.02 to 0.4 gm.atoms/mol. of boron trioxide.

2. A luminescent substance as claimed in Claim 1 wherein the total quantity of activator is from 0.03 to 0.03 gm.atoms/mol. of boron trioxide.

3. A luminescent substance as claimed in Claim 1 or Claim 2 wherein the quantity of gadolinium is from 0.05 to 0.25 gm.atoms/mol. of boron trioxide.

4. A luminescent substance substantially as herein described with reference to any of the compositions defined in Tables I to VI.

5. A luminescent screen containing a luminescent substance as claimed in any preceding claim.

6. A source of radiation containing a luminescent substance as claimed in any of Claims 1 to 4.

7. A method of manufacturing a luminescent substance as claimed in Claim 1 substantially as herein described with reference to the Example.

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